THEORETICA CHIMICA ACTA

Theoret. Chim. Acta (Berl.) 62, 257–263 (1983)

Inclusion of Discrete-to-Continuum Coupling in Multiphoton Excitation and Dissociation Calculations*

I. Harold Zimmerman and Stephen D. Druger

Department of Physics, Clarkson College, Potsdam, New York 13676, USA

Thomas F. George**

Department of Chemistry, University of Rochester, Rochester, New York 14627, USA

A nonperturbative approach to multiphoton excitation and dissociation of molecules is presented in which coupling to the continuum is treated explicitly. Transitions among continuum levels are not modeled directly, but something of their effect is represented by assuming that the continuum population density is so low as to be effectively zero at all times. Two trial applications are briefly discussed.

Key words: Multiphoton excitation – Dissociation – Discrete-to-continuum coupling.

1. Introduction

In this paper we outline a method for modeling IR dissociation of molecules, a method specifically designed to treat coupling to the dissociative continuum of the particle system. The kind of problem we have in mind is that of a molecular system whose negative energy levels are all discrete and whose positive levels form an unbounded continuum to which the discrete levels are coupled by an intense laser field. The discrete states are also coupled to one another, but not

* Research sponsored by the National Aeronautics and Space Administration under Grant No. NSG-2198, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Grant No. AFOSR-82-0046 and the National Science Foundation under Grant No. CHE-8022874. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

** Camille and Henry Dreyfus Teacher-Scholar (1975–1984).

0040-5744/83/0062/0257/$01.40

so the continuum levels. We thus do not include final-state interactions; nor do we attempt to treat the added complications of intramolecular relaxation and conversion processes [1], or predissociation via coupling to other electronic states [2, 3]. For the present we keep our attention focused on how the field may dissociate a molecule for which the only path to breakup is excitation to positive energy levels on a single electronic surface.

In the next section we describe the theory. Following that, we briefly discuss some aspects relating to the scheme's applicability.

2. Theory

To represent the effect of the field we use the familiar semiclassical expression for the interaction. Thus

$$\hat{H}(t) = \hat{H}_0 + 2V \cos(\omega t + \phi_0) \tag{1}$$

is a time-dependent Hamiltonian composed of the field-free particle operator $\hat{H}_0$ and interaction $V \cos(\omega t + \phi_0)$, where

$$V = \vec{\mu} \cdot \vec{E}_0 \tag{2}$$

is the scalar product of the electric dipole moment $\vec{\mu}$ with the field strength vector $\vec{E}_0$. The Schroedinger equation to be solved is then written in dimensionless form as

$$i \frac{\partial}{\partial \phi} \Psi = (\hat{h} + 2v \cos \phi)\Psi, \tag{3}$$

where

$$\phi = \omega t + \phi_0, \tag{4}$$

$$\hat{h} = \hat{H}_0 / \hbar\omega, \tag{5}$$

$$v = V / \hbar\omega, \tag{6}$$

and ω is the angular frequency of the field.

The solution Ψ is expressed as a combination of all particle states:

$$\Psi = \sum_n |n\rangle f_n(\phi) + \int_0^\infty d\varepsilon\, |\varepsilon\rangle f(\varepsilon, \phi). \tag{7}$$

It is the ϕ-evolution of the discrete-level coefficients $\{f_n\}$ that we wish to follow.

Projecting Eq. (3) onto the various particle states yields

$$i \frac{\partial}{\partial \phi} f_n(\phi) = \varepsilon_n f_n(\phi) + 2 \cos \phi \sum_{n'} v_{nn'} f_{n'}(\phi)$$

$$+ 2 \cos \phi \int_0^\infty d\varepsilon\, \langle n|v|\varepsilon\rangle f(\varepsilon, \phi), \qquad \text{(discrete)}; \tag{8a}$$

$$i\frac{\partial}{\partial\phi}f(\varepsilon,\phi)=\varepsilon f(\varepsilon,\phi)+2\cos\phi\sum_{n'}\langle\varepsilon|v|n'\rangle f_{n'}(\phi)$$

$$+2\cos\phi\int_0^\infty d\varepsilon'\,\langle\varepsilon|v|\varepsilon'\rangle f(\varepsilon',\phi),\qquad\text{(continuum)}.\tag{8b}$$

Since the effect of coupling among continuum levels on the bound-state coefficients is assumed negligible, we approximate by dropping the integral term from the right of Eq. (8b). This leaves

$$i\frac{\partial}{\partial\phi}f(\varepsilon,\phi)=\varepsilon f(\varepsilon,\phi)+2\cos\phi\sum_{n'}\langle\varepsilon|v|n'\rangle f_{n'}(\phi),$$

which integrates to yield

$$f(\varepsilon,\phi)=-2i\sum_{n'}\langle\varepsilon|v|n'\rangle\int_{\phi_0}^{\phi}d\phi'\,e^{-i\varepsilon(\phi-\phi')}\cos\phi' f_{n'}(\phi').\tag{9}$$

This is zero at $\phi=\phi_0$, so that the correct boundary condition is observed. Therefore we can substitute directly for $f(\varepsilon,\phi)$ in Eq. (8a) to find

$$i\frac{\partial}{\partial\phi}f_n(\phi)=\varepsilon_n f_n(\phi)+2\cos\phi\sum_{n'}v_{nn'}f_{n'}(\phi)$$

$$-4i\cos\phi\sum_{n'}\int_{\phi_0}^{\phi}d\phi'\,\nu_{nn'}(\phi-\phi')\cos\phi' f_{n'}(\phi'),\tag{10}$$

where [4]

$$\nu_{nn'}(\theta)=\int_0^\infty d\varepsilon\,\langle n|v|\varepsilon\rangle\,e^{-i\varepsilon\theta}\langle\varepsilon|v|n'\rangle,\tag{11a}$$

$$=\langle n|v\hat{u}(\theta)v|n'\rangle-\sum_l v_{nl}\,e^{-i\varepsilon\theta_l}v_{ln'}.\tag{11b}$$

The operator $\hat{u}(\theta)$ is

$$\hat{u}(\theta)\equiv e^{-i\hat{h}\theta}.\tag{12}$$

Before we can hope to solve Eq. (10) we must have an integrated expression to replace the integral. This in turn requires that functional forms be available to represent $\nu_{nn'}$ and $f_{n'}$ in the integrand. The first of these we replace by its $\theta=0$ value:

$$\nu_{nn'}(\theta)\to\nu_{nn'}\equiv\nu_{nn'}(0)=(v^2)_{nn'}-\sum_l v_{nl}v_{ln'}.\tag{13}$$

This is the value of $\nu_{nn'}$ when the continuum is empty, indicating that the effect of this approximation will be to maximize the rate of loss from the discrete levels.

With this approximation we find for Eq. (10)

$$i\frac{\partial}{\partial\phi}f_n(\phi)=\varepsilon_n f_n(\phi)+2\cos\phi\sum_{n'}v_{nn'}f_{n'}(\phi)$$
$$-4i\cos\phi\sum_{n'}\nu_{nn'}\int_{\phi_0}^{\phi}d\phi'\cos\phi' f_{n'}(\phi'). \tag{14}$$

In matrix notation this becomes

$$i\dot{\boldsymbol{f}}(\phi)=\boldsymbol{W}(\phi)\boldsymbol{f}(\phi)-4i\cos\phi\,\mathbf{v}\boldsymbol{I}(\phi,\phi_0), \tag{15}$$

where the dot signifies differentiation with respect to ϕ and where

$$\boldsymbol{W}(\phi)=\mathscr{E}+2\boldsymbol{v}\cos\phi,\qquad \mathscr{E}_{nn'}=\delta_{nn'}\varepsilon_n; \tag{16}$$

$$\boldsymbol{I}(\phi,\phi_0)=\int_{\phi_0}^{\phi}d\phi'\cos\phi'\boldsymbol{f}(\phi'). \tag{17}$$

We then express the integral as the sum of two parts, writing

$$\boldsymbol{I}(\phi,\phi_0)=\boldsymbol{I}(\phi,\phi_\alpha)+\boldsymbol{I}(\phi_\alpha,\phi_0). \tag{18}$$

The second quantity on the right is known. The first is solved under the assumption that $\phi-\phi_\alpha$ is a small quantity:

$$\boldsymbol{I}(\phi,\phi_\alpha)\equiv\int_{\phi_\alpha}^{\phi}d\phi'\cos\phi'\boldsymbol{f}(\phi')$$
$$\cong\frac{\phi-\phi_\alpha}{2}[\cos\phi\boldsymbol{f}(\phi)+\cos\phi_\alpha\boldsymbol{f}(\phi_\alpha)]. \tag{19}$$

Substituting into Eq. (15) and using Eqs. (18) and (19) yields, upon multiplying through by $-i$,

$$\dot{\boldsymbol{f}}=-i\boldsymbol{\Lambda}(\phi)\boldsymbol{f}-2\cos\phi\,\mathbf{v}[(\phi-\phi_\alpha)\cos\phi_\alpha\boldsymbol{f}_\alpha+2\boldsymbol{I}_\alpha]. \tag{20}$$

Left unlabeled, $\boldsymbol{f}$ denotes $\boldsymbol{f}(\phi)$, while $\boldsymbol{f}_\alpha=\boldsymbol{f}(\phi_\alpha)$ and $\boldsymbol{I}_\alpha=\boldsymbol{I}(\phi_\alpha,\phi)$. The array $\boldsymbol{\Lambda}(\phi)$ is given by

$$\boldsymbol{\Lambda}(\phi)=\boldsymbol{W}(\phi)-2i(\phi-\phi_\alpha)\cos^2\phi\,\mathbf{v}. \tag{21}$$

Eq. (20) is the working equation of the method, forming the basis for a propagation which we carry out using a modification of the Magnus technique [5–7]. Given $\boldsymbol{f}_\alpha$ and $\boldsymbol{I}_\alpha$ we compute $\boldsymbol{f}$ as

$$\boldsymbol{f}(\phi)=e^{-i\boldsymbol{\Lambda}_\alpha(\phi-\phi_\alpha)}\boldsymbol{f}_\alpha-2\int_{\phi_\alpha}^{\phi}d\phi'\cos\phi'\,e^{-i\boldsymbol{\Lambda}_\alpha\cdot(\phi-\phi')}\mathbf{v}[(\phi'-\phi_\alpha)\cos\phi_\alpha\boldsymbol{f}_\alpha+2\boldsymbol{I}_\alpha]. \tag{22}$$

Using this result in Eqs. (19) and (18) then yields $\boldsymbol{I}(\phi)$ which, together with $\boldsymbol{f}(\phi)$, becomes the input for the next step. For $\boldsymbol{\Lambda}_\alpha$ in Eq. (22) we may use

$$\boldsymbol{\Lambda}_\alpha=\boldsymbol{\Lambda}[\tfrac{1}{2}(\phi+\phi_\alpha)], \tag{23}$$

provided the interval $\phi-\phi_\alpha$ be small enough.

In actual practice the matrix $\mathbf{\Lambda}_\alpha$ is diagonalized before exponentiating, so as to ease the task of evaluating $e^{-i\mathbf{\Lambda}_\alpha\theta}$. The diagonal exponential is then "undiagonalized" to render the matrix consistent with the original basis set. In the present instance we see that diagonalization will not be so easy as in the usual case where the $\mathbf{\Lambda}_\alpha$-array is Hermitian; however, it is still a time-saving step.

The result of doing a calculation such as outlined here will be a set of probability amplitudes $\{f_n(\phi)\}$ whose squares in absolute value will give the probability that a discrete particle state $|n\rangle$ is occupied at time t:

$$P_n(t) = |f_n(\phi = \omega t + \phi_0)|^2. \tag{24}$$

Furthermore, because of coupling to the continuum, there will be loss from the discrete spectrum so that $\sum_n P_n(t) < 1$ in general. The rate of such loss, monitored as a function of time, will yield useful information as to the way in which probability flows out of the resolvable spectrum of a molecular system exposed to intense laser radiation.

3. Discussion

We have outlined a method for modeling multiphoton excitation and dissociation of molecules which is designed to treat cases in which only one electronic surface is involved, or more specifically, cases in which all potential energy surfaces have a common asymptotic value which we take to be the zero reference of our energy scale. Generalization to include refinements such as radiationless decay and other intramolecular processes should in principle be no more difficult with this method than with any other. Our reason for working out the present approach is to include coupling to the continuum in a fundamentally rigorous way. We have made approximations that to some extent vitiate the formal exactness of the theory as originally summarized in Eqs. (10–12), but that seems to be the price we must pay for a useable method.

The theory should also be useable in situations where a quasicontinuum replaces the low-energy portion of the continuum, provided the density of states is sufficiently great that no one part of the quasicontinuum becomes significantly populated. We note that bottle-necking in the quasicontinuum is not likely to occur.

Finally, we point out that only those discrete levels lying within a few photons of the continuum need be coupled to it. Thus the dimensionality of the matrix $\mathbf{v}$ will be much smaller than $\mathbf{V}$. This should ease the task of applying the theory when a large number of discrete levels are involved.

We have tried the method out on two Morse oscillators, one chosen to mimic the ground electronic surface of HCl and the other modified as we shall describe shortly. The particle Hamiltonian is then

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + D[e^{-2\beta(r-r_{eq})} - 2e^{-\beta(r-r_{eq})}], \tag{25}$$

where D is the well depth, r is the vibrational coordinate, r_{eq} is the equilibrium point, and β is the fall-off parameter. The HCl model surface supports 24 vibrational states when constructed using data from Herzberg [8]. A dipole moment function $\mu(r)$, r the internuclear separation, can be written in the form

$$\mu(r) = \sum_{n=0}^{3} a_n r^n e^{-\gamma r} \tag{26}$$

with the constants γ and $\{a_n\}$ determined by fitting this function and its first four derivatives, evaluated at the equilibrium separation r_{eq}, to the tabulated data of Kaiser [9]. Coupling among the vibrational levels occurs through the interaction of the imposed field and this dipole moment. A number of candidate fields have been employed, all of very high intensity ($\sim 10^{14}$ W/cm^2), but even with the optimal choice, significant excitation is seen only to $v = 5$ or 6; beyond that, the maximum observed probability falls off exponentially with increasing v so that virtually no occupation occurs for states above $v = 10$. Dissociation after 100 cycles of the field is less than 10^{-8}.

This result is not particularly surprising. It is well known that diatomic molecules do not dissociate in the presence of single-mode *IR* fields. The usual explanation is that the density of states does not increase sufficiently to overcome the detuning that results from the anharmonicity of the well. Including rotational degrees of freedom might change this result to some extent, but on the evidence we should not expect the change to be significant [10].

The second Morse oscillator ($D = .121$, $\beta = r_{eq} = \sqrt{2}$, all in atomic units) exhibits just eleven bound states. The dipole moment operator $\mu(r)$ and the field intensity are the same as before. In this case dissociation does occur; after 100 oscillations of the field (whose quantum is resonant with the $v = 1 \rightarrow v = 2$ transition) we see a probability of 0.024 for loss to the continuum. Because the model is so artificial we do not describe its evolution in any detail, but one interesting phenomenon is worth noting. The dissociation occurs in steps. There is no loss until higher-lying levels ($v \cong 8$ to 11) become populated. Dissociation then proceeds until these levels become depopulated once more as a result of stimulated absorption into the continuum together with stimulated emission back to lower levels. This behavior repeats cyclically in the current model, at least for the relatively short periods of time considered here. We should expect eventual scrambling of the excitation–deexcitation pattern, but over short times the system behaves quite regularly, leading to the observed steplike pattern of dissociation as a function of time.

Future research in two directions is indicated. First, the present method ought to be applied to more complicated particle systems so as to ascertain its potential for treating problems of current interest, such as the multiphoton dissociation of SF_6 for example. Second, the method needs to be modified so as to more nearly reflect the true time-dependence of the matrix $\mathbf{v}(\theta)$. An important effect that we wish to examine in this regard is the possibility of stimulated emission from the continuum back to discrete levels. When we replaced $\mathbf{v}(\theta)$ by $\mathbf{v} = \mathbf{v}(0)$,

we essentialty said that the continuum never became populated. This approximation also needs to be tested. We should, however, note our belief that the approximation is likely to be accurate in that it represents (in a highly imprecise way) the possibility of rapid transitions to high-lying continuum levels, thus adjusting somewhat for errors introduced when continuum–continuum interactions are neglected.

Acknowledgments. One of us (I.H.Z.) wishes to acknowledge instructive conversations with personnel of the NASA-Ames Research Center's Computational Chemistry Group at Moffet Field, California, with especial thanks to Drs. J. R. Stallcop, B. C. F. M. Laskowski and J. O. Arnold. Thanks also to Dr. A. Komornicki who was his host during his visit there.

References

1. Mukamel, S., Jortner, J.: Chem. Phys. Letters **40**, 150 (1976); Black, J. G., Yablonovich, E., Bloembergen, N., Mukamel, S. Phys. Rev. Letters **38**, 1131 (1977); Cantrell, C. D. Galbraith, H. W.: Opt. Comm. **18**, 513, (1976)
2. Bandrauk, A. D., Child, M. S.: Mol. Phys. **19**, 95 (1970); Caplan, C. E., Child, M. S.: Mol. Phys. **23**, 249, (1972)
3. Zimmerman, I. H., Yuan, J. M., George, T. F.: Mol. Phys. **36**, 1675 (1978); Yuan, J. M., George, T. F.: J. Chem. Phys. **68**, 3040 (1978)
4. Jordan, T. F.: Linear operators for quantum mechanics. New York: Wiley, 1969
5. Walker, R. B., Preston, R. K.: J. Chem. Phys. **67**, 2017, (1977)
6. Magnus, W.: Commun. Pure Appl. Math. **7**, 649, (1954)
7. Light, J. C.: Methods of computational physics 10, 111, Ed. Rotenberg, M.: New York: Academic, 1971
8. Herzberg, G.: Spectra of diatomic molecules, 534, New York: Van Nostrand Reinhold, 1950
9. Kaiser, E. W.: J. Chem. Phys. **53**, 1686 (1970)
10. Faisal, F. H. M., Rahman, N. K.: Nuovo Cimento B **13**, 114 (1973); Miranda, L. C. M.: Phys. Letters A **56**, 374 (1976)

Received June 20, 1982